Towards Accurate and Efficient Predictions of Martensitic Transition Temperatures for Shape Memory Alloys from First Principles

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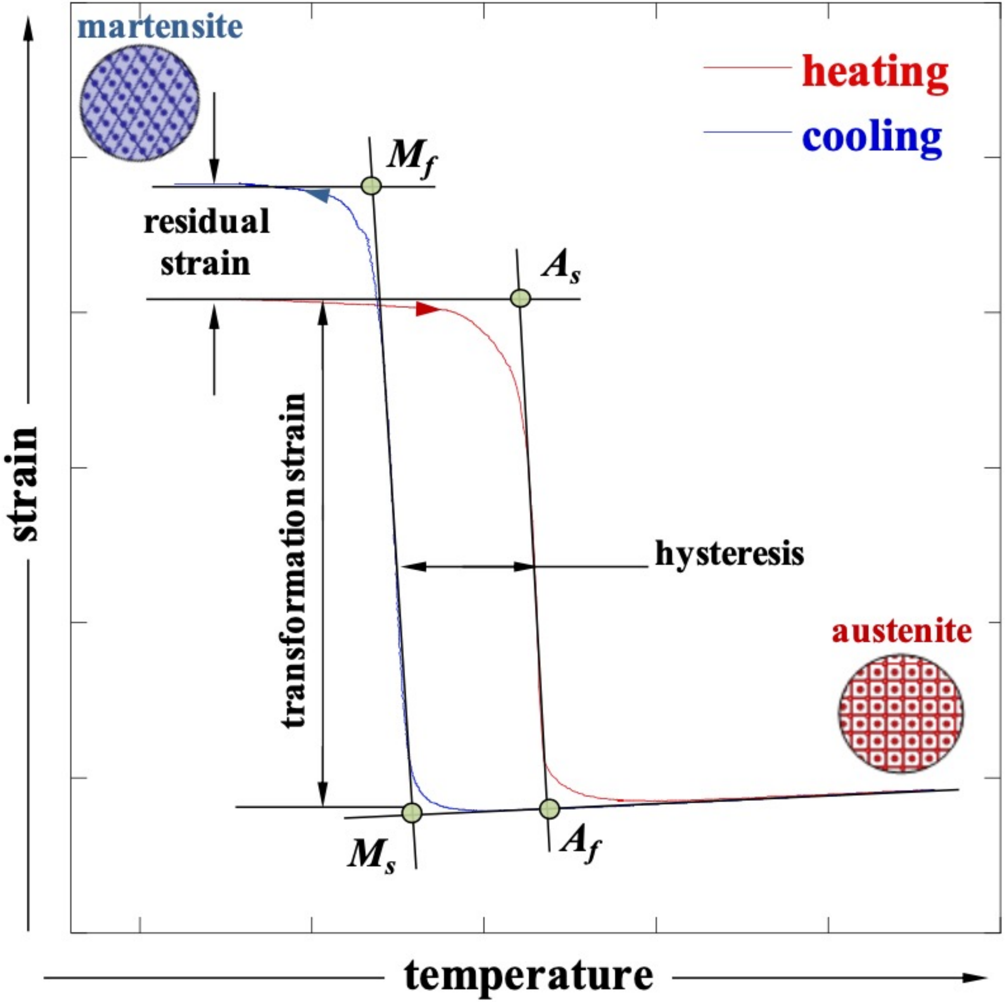
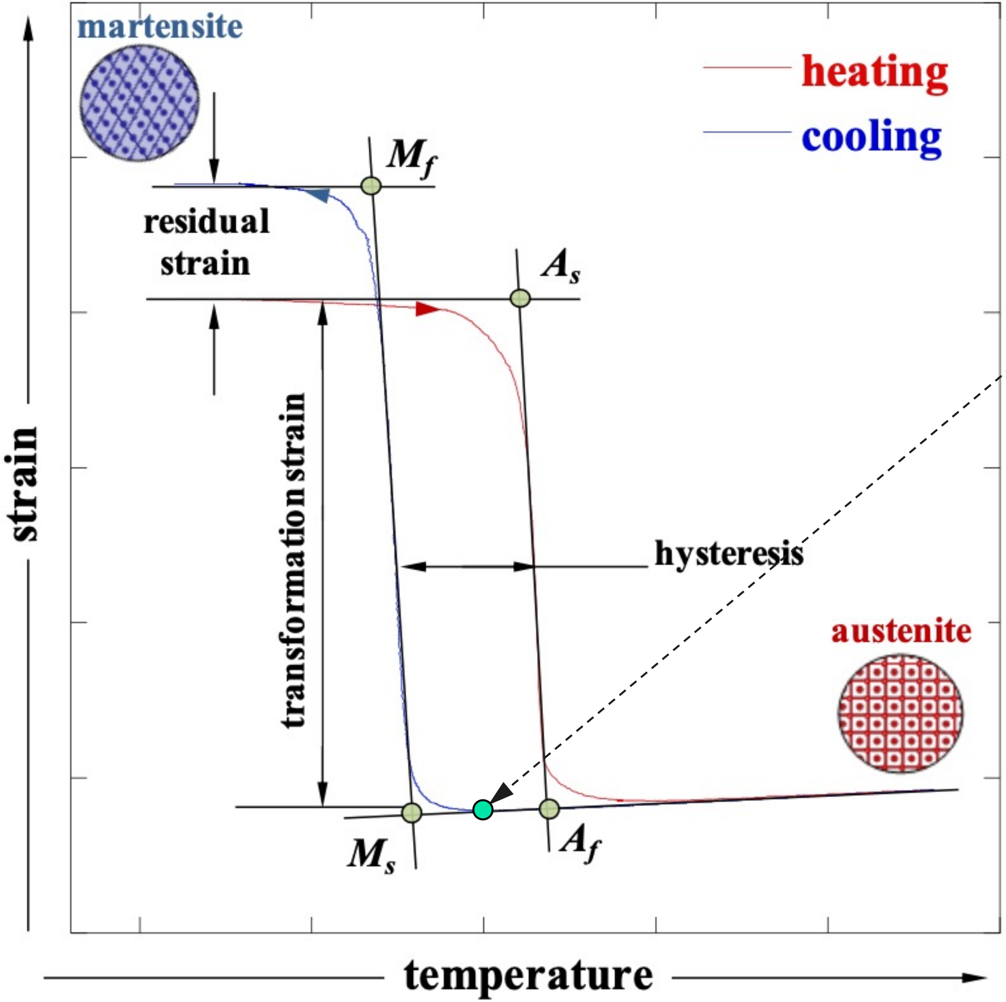


- **Shape memory alloys** (SMAs) can remember and recover their original shapes upon heating.
- **Reversible** martensitic phase transition between austenite and martensite phases.
- SMA-based **actuators** are superior to conventional actuators.
- However, the martensitic transition temperatures (**MTT**s) are limited by available binary SMAs (e.g., NiTi).
- MTT can be well tuned in complex ternary and quaternary SMAs, calling for **computational design**.



Expt: Measuring characteristic T such as martensite starting (M_s) and austenite finish (A_f)

$(M_s + A_f)/2 =$ **MTT**

Theory: find the stable phase with the minimum free energy (G):

$$G = \mathrm{E} + \mathrm{ECFE} + \mathrm{HFE} + \mathrm{AHFE}$$

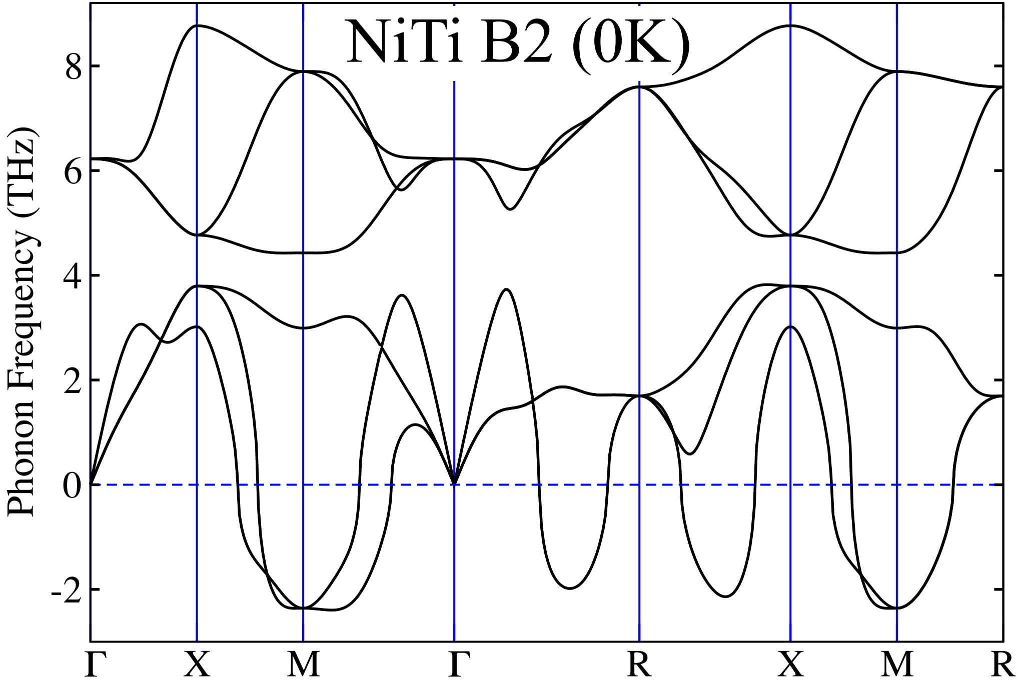
E: electronic energy

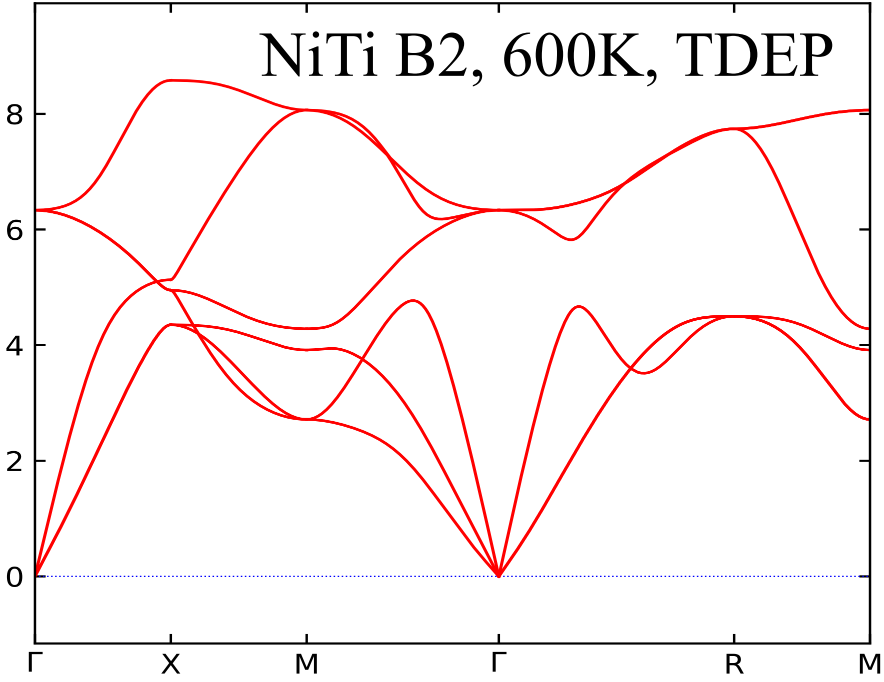
ECFE: electronic config. FE

HFE: harmonic phonon FE

AHFE: anharmonic phonon FE

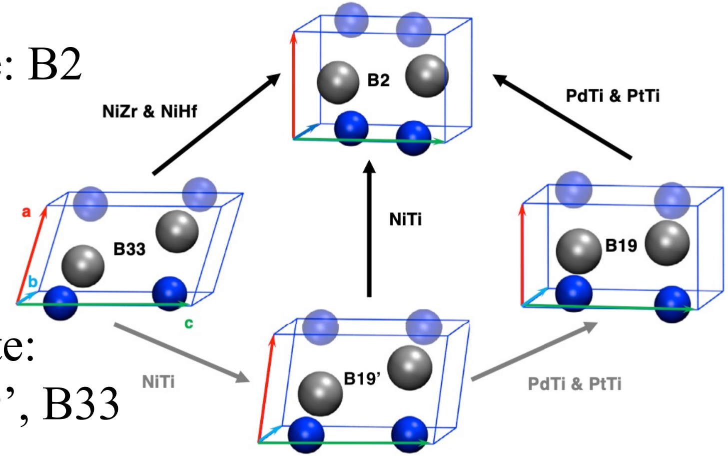
- At low T, austenite B2 phase is not stable due to imaginary (negative) phonons.
- High T stabilizes B2 but **AHFE** is substantial.
- **Challenge**: Computationally very demanding to obtain AHFE, while accurate MTT prediction requires AHFE within ~ meV/atom.

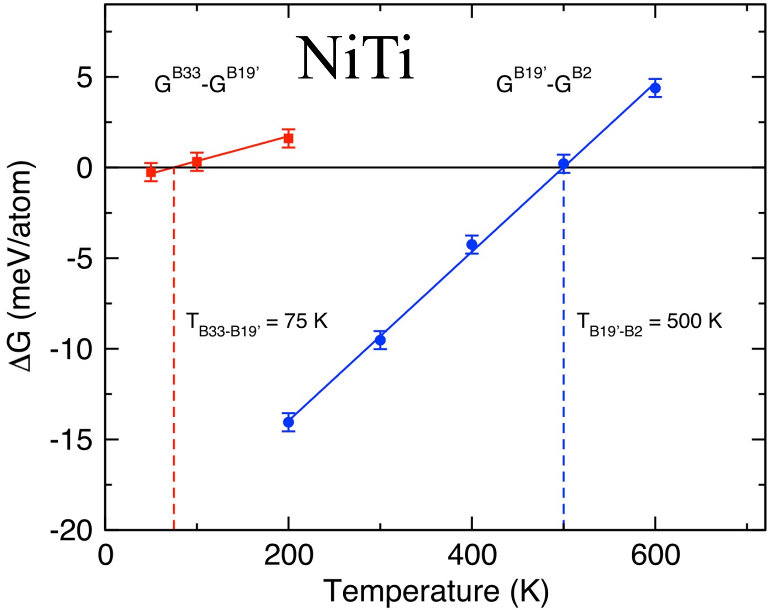




Austenite: B2

Martensite:
B19, B19', B33





Thermodynamics integration (TI) to obtain

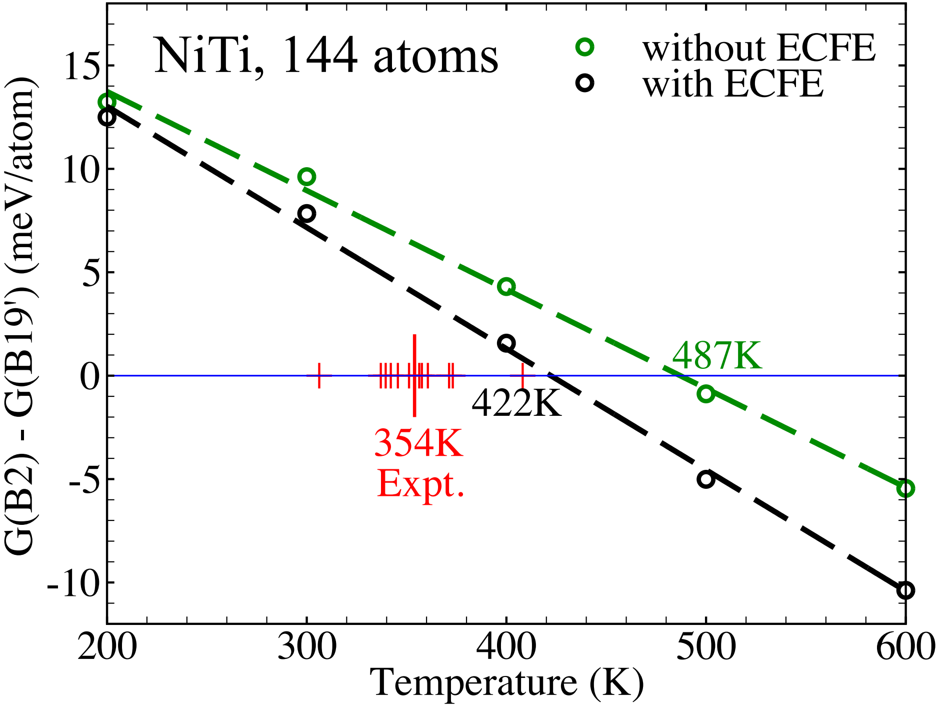
$$\mathrm{AHFE} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda$$

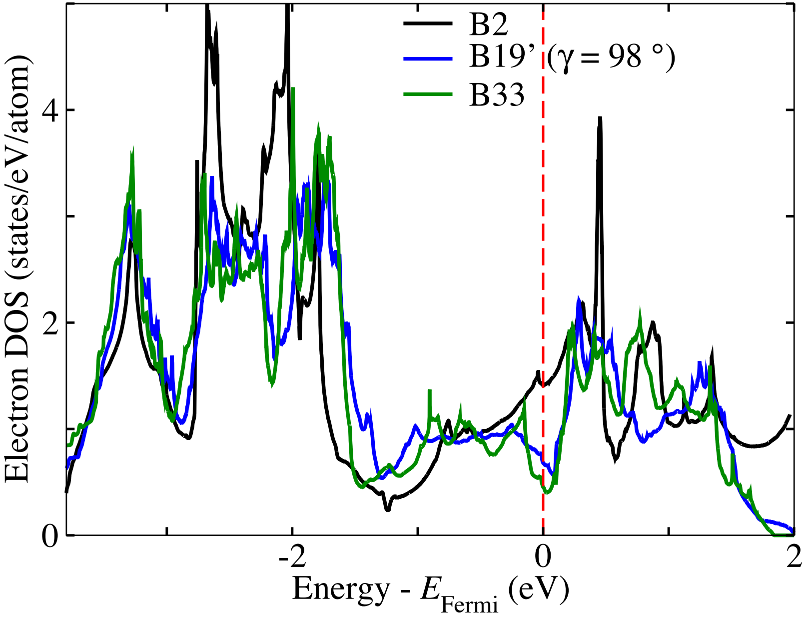
$\lambda = 0$: harmonic potential
$\lambda = 1$: DFT potential

- **Previously** *ab initio* TI was only applied to study simple binary SMAs.
- MTT of NiTi was predicted to be between 482 K (AM 2021) and 500 K (PRB 2016), compared with measured 354 K.
- B33 phase of NiTi was never observed at low T, inconsistent with theory.

Haskins *et al*., PRB **94**, 214110 (2016)
Haskins *et al*., Acta Mater. **212**, 116872 (2021)

$$G = E + \mathrm{HFE} + \mathrm{AHFE} + \mathbf{ECFE}$$





- **UP-TILD** reduces computational cost by one to two orders w/o losing accuracy in AHFE.
- Including **ECFE** reduces MTT by 65 K for NiTi.

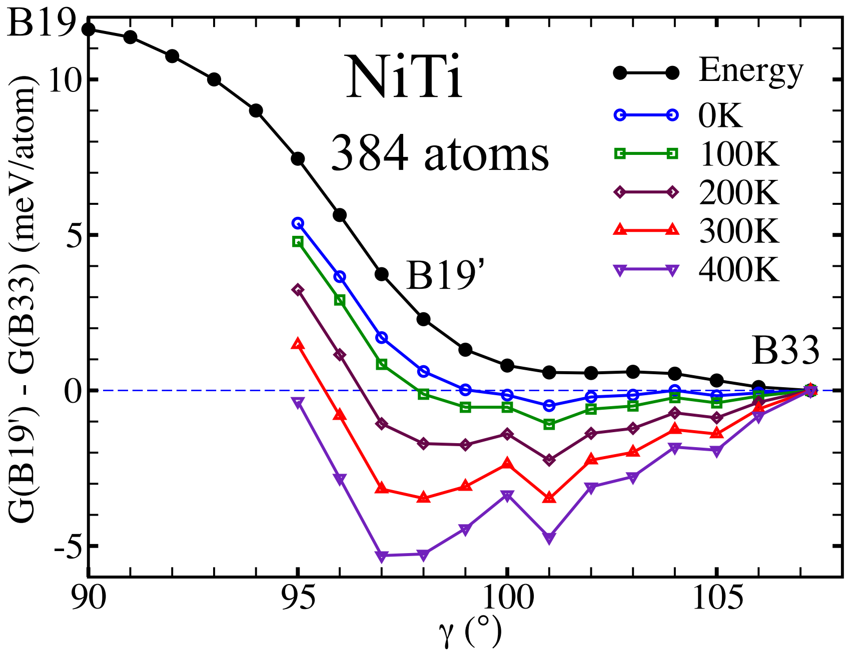
- Electron DOS at E_F of B2 is much larger than that of B19' in NiTi.
- ECFE in B2 is more negative.

$$\mathrm{ECFE} = U^{\mathrm{el}}_{\mathrm{DOS}}(T) - T\,S^{\mathrm{el}}_{\mathrm{DOS}}(T)$$

- Compute DOS of 10-20 MD snapshots at each T where TI is carried out.

Low-Temperature Phase of NiTi

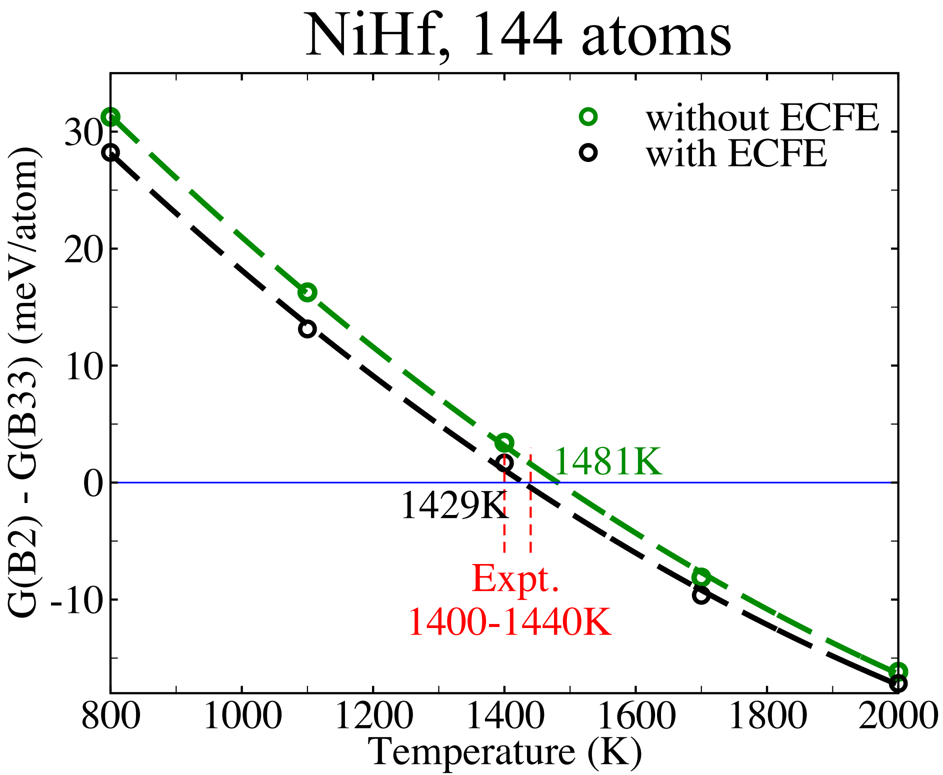
- When T ≲ 600 K and size of supercell ~ 400 atoms, the AHFE is negligible for stable phases (B19' and B33) of SMAs, and the quasi-harmonic approximation (QHA) is valid.
- Previous calculations didn't reach convergence for phone FE at low T when TI is not applicable.
- No transition from B19' to B33 in NiTi; B19' is more stable than B33 even at 0 K.

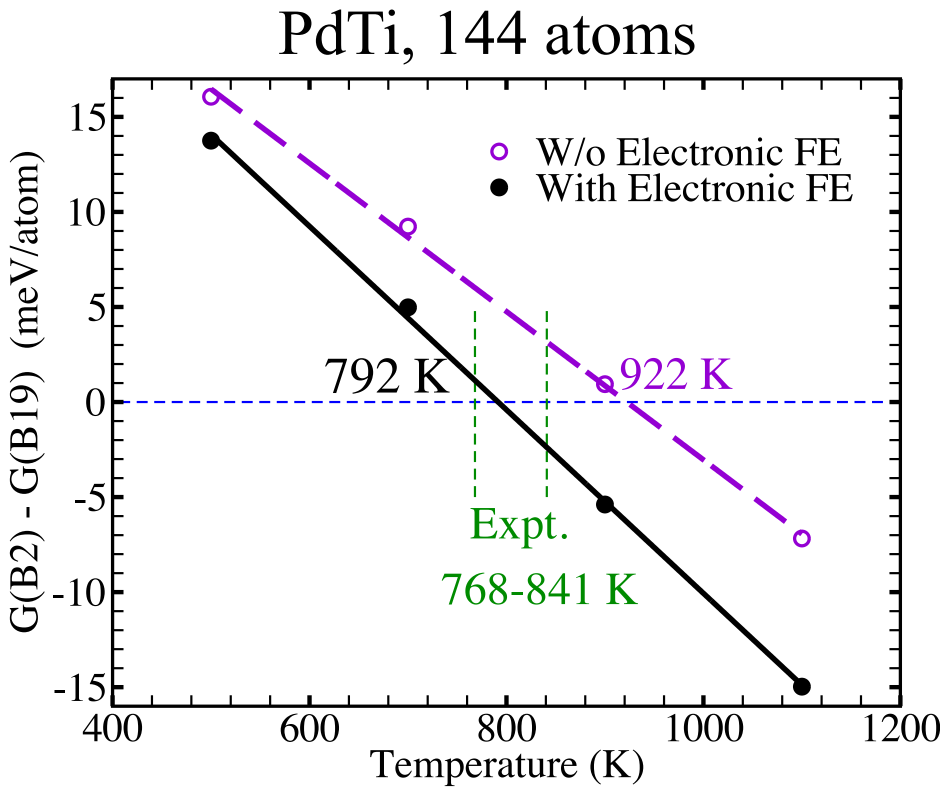


600K, phonon FE in meV/atom

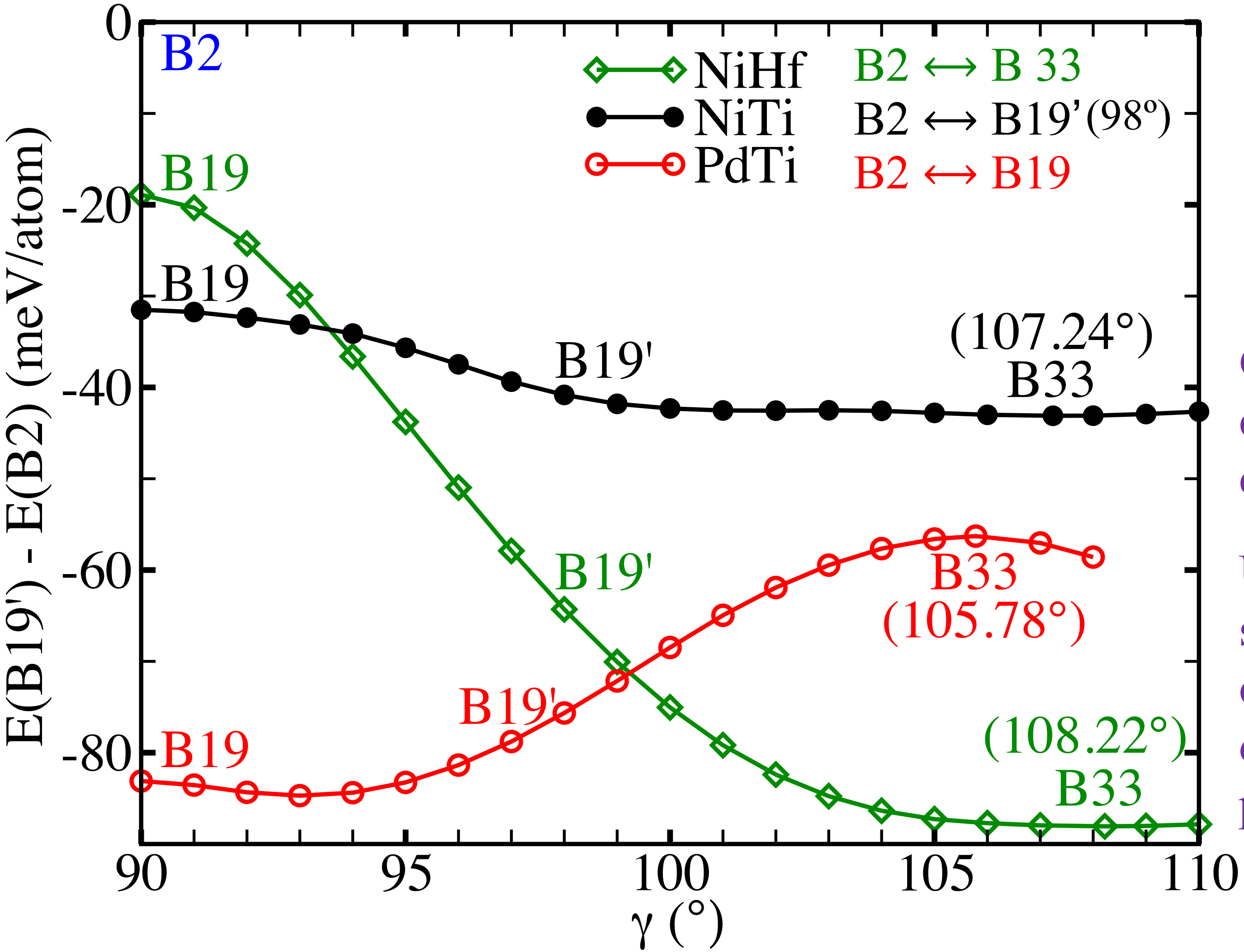
	HFE	AHFE	FE(tot)
B2 (144)	-150.7	-43.2	-194.9
B2 (384)	-169.5	-25.6	-195.1
B19'(144)	-132.0	-14.2	-146.2
B19'(384)	-145.7	**-0.16**	-145.9

(number of atoms in supercell)





- Including ECFE reduces MTT by 52 K for NiHf and 108 K for PdTi, in better agreement with experimental data.

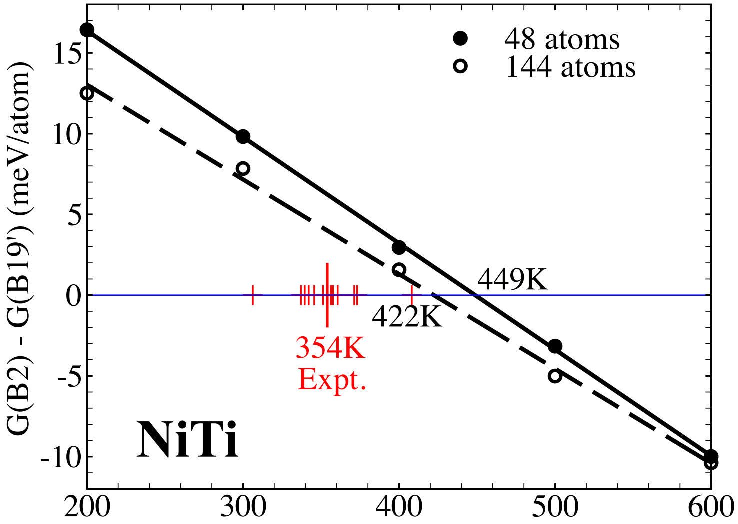


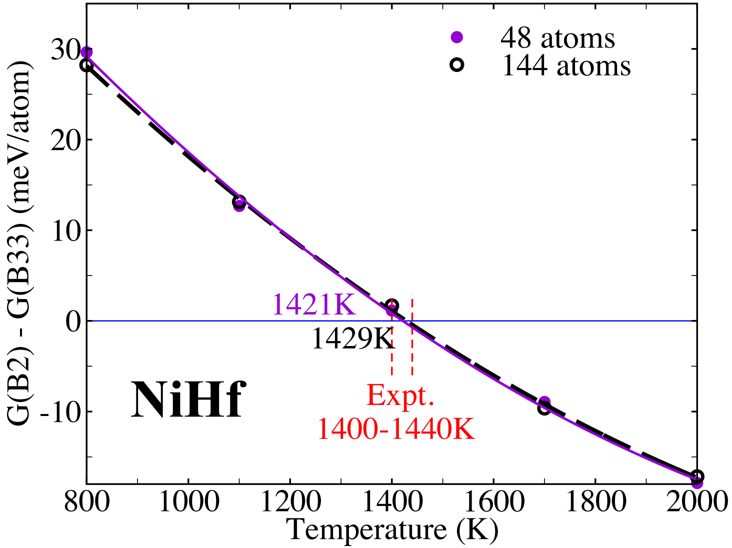
Ternaries:

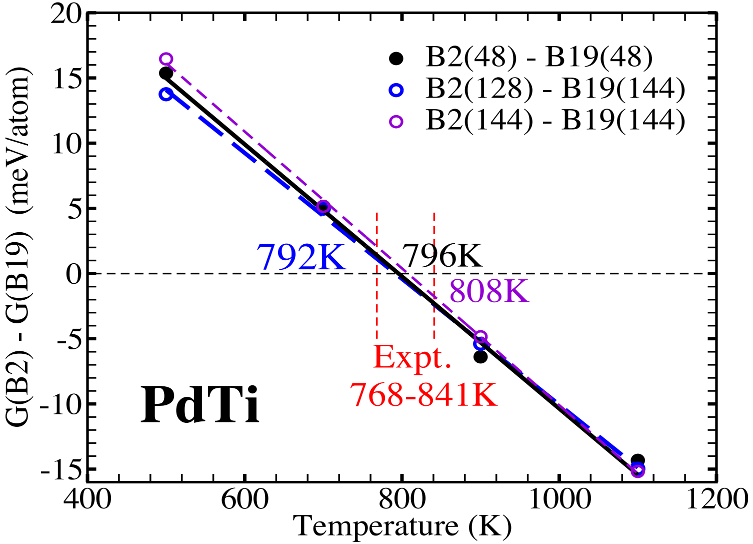
- $Ni_{0.5}Ti_{0.5-x}Hf_x$
- $Pd_xNi_{0.5-x}Ti_{0.5}$

Challenge: Numerous compositions and combinations.

Using 144-atom-supercell is computationally very demanding. Not practical for ternaries.

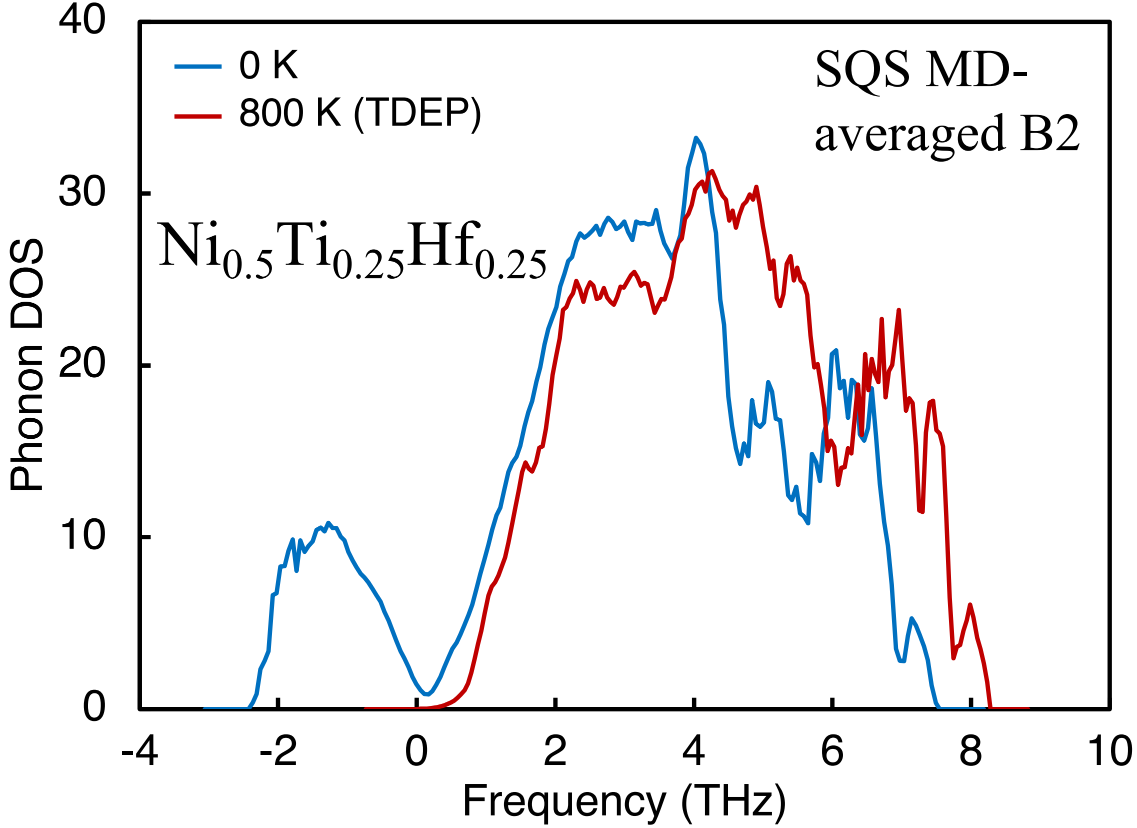


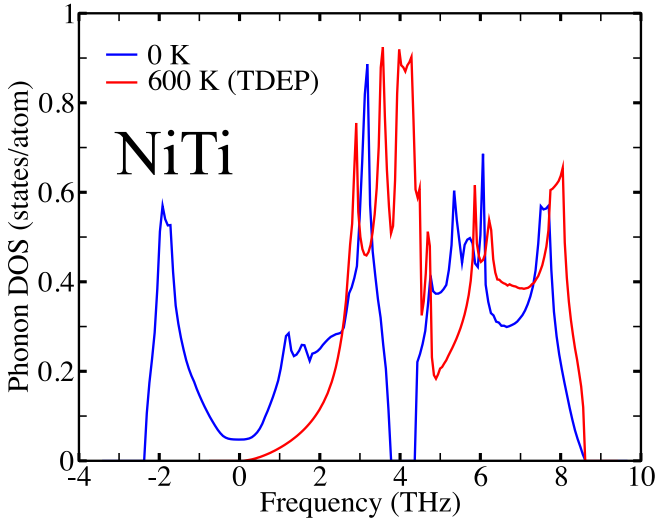


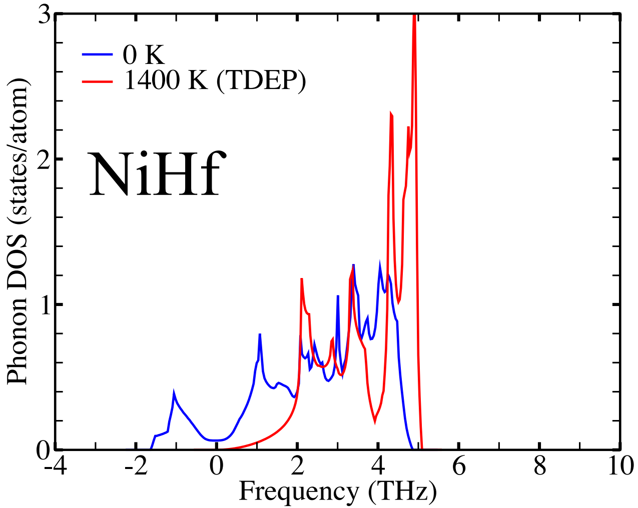


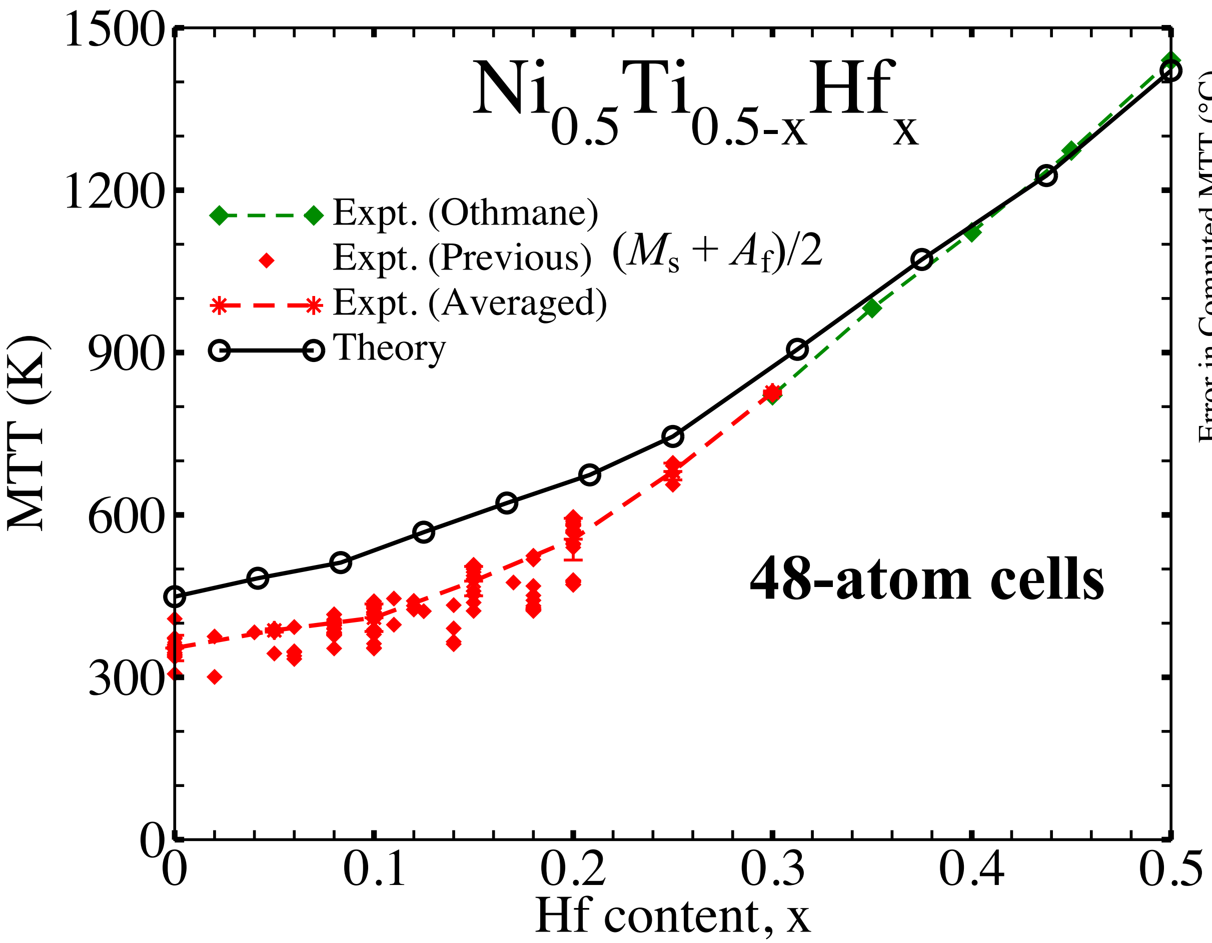
- Predicted MTTs using 48-atom supercells in binaries are close to those using 144-atom supercells (converged MTT).
- Using 48-atom supercells in ternaries reduces computational cost by ~ 20 folds.

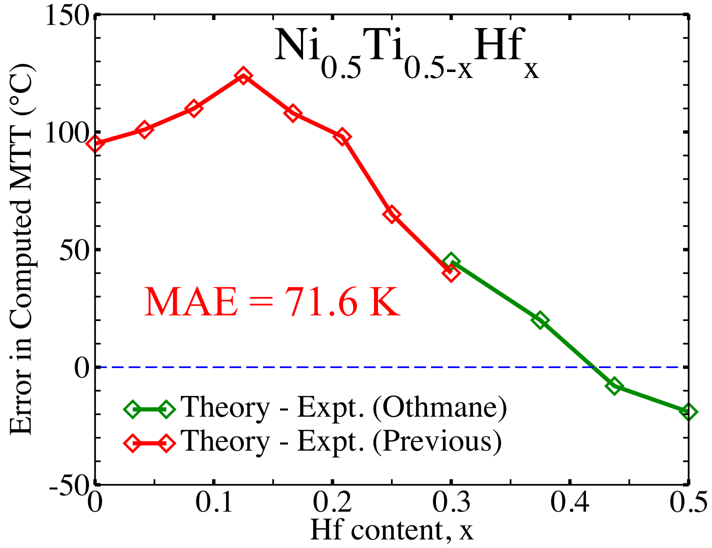
SQS: **s**pecial **q**uasi-random **s**tructures:
most probable alloys (disordered)



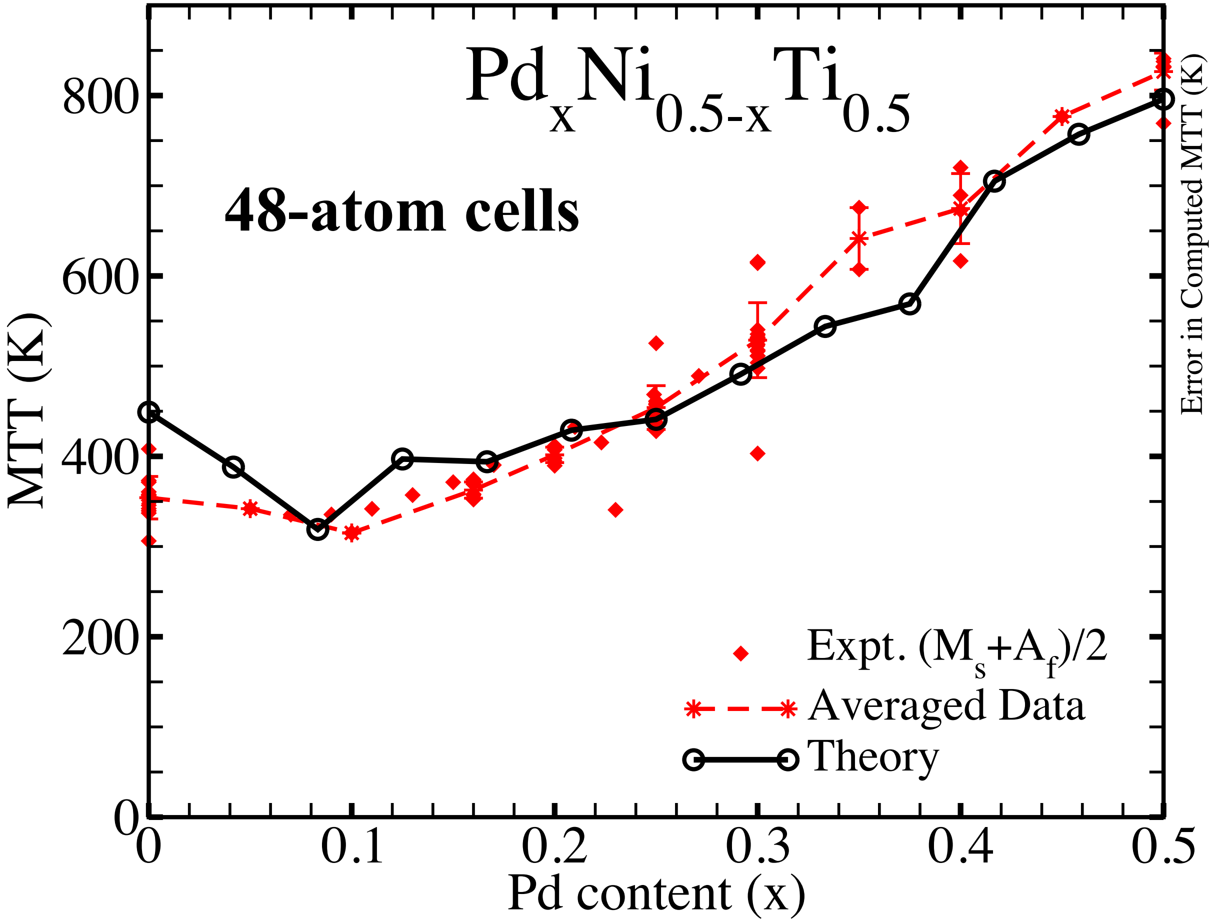


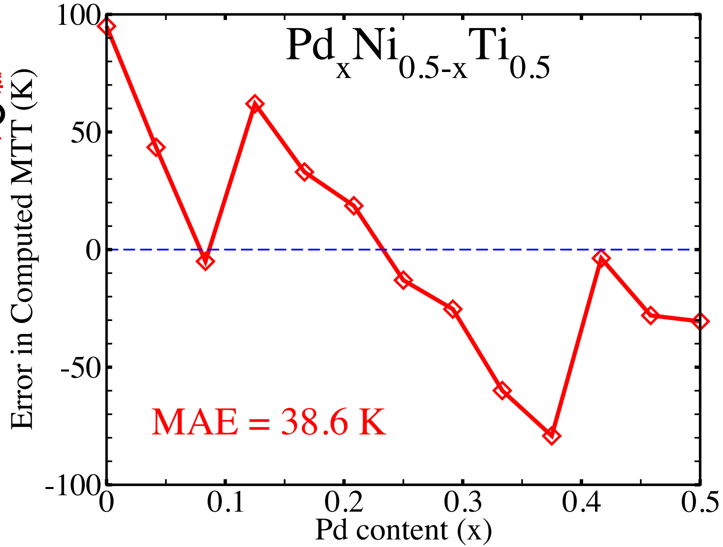






- Excellent agreement with recent measurements ($x \geq 0.3$) by NASA scientists.
- For $x \leq 0.2$, MTTs are overestimated by ~ 100 K, similar to that in NiTi (using 48 atoms).

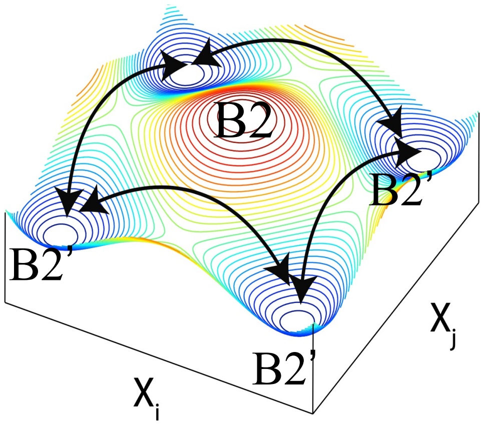




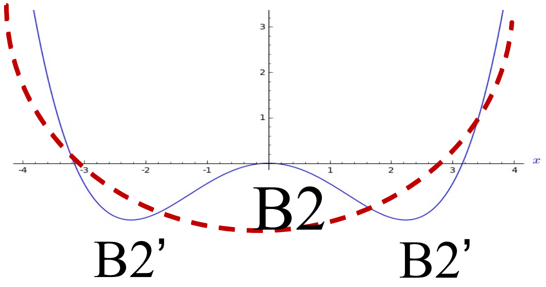
- Very good agreement with measured data.
- *Pure* cell-size effect can be estimated from end binaries.
- Cell size also affects the SQS structure – **a challenge**.

Summary and Future Work

- First-principles calculations can accurately predict martensitic transitions in SMAs.
  - Including ECFE reduces error in predicted MTT
  - Solved the controversy of the B33 phase in NiTi
  - Applicable to ternary SMAs: the computed MTTs are within about 100 K compared with experiment



- Thermodynamics integration is too expensive
  - Further improve TI
  - P4 method: finding all local minima (B2')
  - Analytical methods up to 6th-order Tylor expansion



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